

CEPC Control Notice to Program Only

(21) (A1)	2,110,461
(22)	1993/12/01
(43)	1994/07/26

(51) INTL.CL. 5 C23F-011/00; C23F-011/18

(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Composition and Methods for Inhibiting the Corrosion of Low Carbon Steel in Aqueous Systems

(72) Zefferi, Suzanne M. - U.S.A. ; Rodzewich, Edward A. - U.S.A. ;

(71) Betz Laboratories, Inc. - U.S.A. ;

(30) (US) 08/007,943 1993/01/25

(57) 18 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.

Canadä

ABSTRACT

Methods and composition corrosion of low carbon steel in The compositions comprise a combination of a hydrolyzable group a complex fluoro acid.

e provided for inhibiting the ntact with an aqueous system. From of a silicon compound sched to an Si-O grouping and

Z-S11

COMPOSITION AND METHOD FOR INHIBITING THE CORROSION OF LOW CARSON STEEL IN AQUEOUS MEDIUMS

FIELD OF THE INVENTION

The present invention relates to compositions and methods of providing a durable, long lasting chemically resistant corrosion inhibiting film on the surface of low carbon steel.

BACKGROUND OF THE INVENTION

In aqueous systems, particularly industrial aqueous systems, metallic parts need to be protected from corrosion and corrosion by-products. The metallic parts of these systems which are exposed to the aqueous fluid could include heat exchangers, boilers, pipes, engine jackets, and the like. The cooling fluid contains aggressive ions which are often corrosive towards these metal parts. The introduction of oxidizing substances for biological control will increase the aggressiveness of the cooling fluid toward the metal parts. Corrosion inhibitors are generally added to the aqueous system to prevent metal loss, and pitting.

The use of conventional corrosion inhibitors have certain disadvantages. Chromates, are efficacious as corrosion inhibitors, but are known to be very toxic. Zinc has solubility limitations and has also been shown to be toxic to aquatic life. Phosphates and organophosphonates can lead to scale and deposition unless effective deposit control agents are added and well controlled. In addition, phosphorus containing compounds, while not directly toxic to aquatic life, can promote environmental problems such as eutrophication of surface waters. There currently exists a great need for non-chromate, non-phosphorus corrosion inhibiting treatments.

SUMMARY OF THE INVENTION

10

15

20

The invention relates to compositions and methods of providing a durable, long lasting chemically resistant corrosion inhibiting film on the surface of low carbon steel.

These aqueous solutions are dilute and are carried to the LCS surface via the aqueous media and react with the surface in contact with the aqueous media. Unlike a traditional conversion coating process, the aqueous solution is never dried and a second coating, such as paint, is not necessarily required.

DESCRIPTION OF THE RELATED ART

- U.S. 4,744,950, Hollander, teaches methods for inhibiting copper corrosion in cooling water systems. Alkyl benzotriazole compounds provide a lasting film on the copper surfaces in contact with the aggressive waters of an open cooling water system.
- U.S. 4,303,568, May et al., teaches methods and compositions for inhibiting the corrosion of ferrous metals in contact with aqueous systems. A passive oxide film can be formed on the ferrous surfaces by adding a composition which comprises a polymer of acrylic moieties and hydroxylated lower alkyl acrylate moieties, and a water soluble orthophosphate.

DETAILED DESCRIPTION OF THE INVENTION

20

The present invention relates to compositions and methods of providing a durable lengtheting chemically resistant corresion inhibiting film on the surface of low carbon steels comprising adding to said steels an effective amount of an aqueous solution of a silicon compound containing a hydrolyzable group attached to a Si-O grouping and complex fluoro acid.

It has been discovered that low concentrations of silicon compounds and fluorozirconic acid form a tenacious film or coating on the surfaces of low carbon steels. The formation of

this protective coating or film utilizing silicon compounds needs no drying or direct application steps. This corrosion inhibition is achieved with no other corrosion inhibitor present.

Ine silicon compounds usefil in this invention can be selected from silicon compounds containing Si-O bonds that are attached to a group that is easily hydrolyzed such as an alkoxy. Inorganic silicates also have Si-O bonds with easily hydrolyzed inorganic salts attached. Representative compounds include

N-(& -aminoethyl) - y - aminopropyltrimethoxysilane which is commercially available from Oow Chemical Corporation as Z-6020, methyltriacetoxysilane and -aminopropyltriethoxysilane, both available from Huls, and sodium silicate. The inventors anticipate that any compound containing a hydrolyzable group attached to a Si-O grouping will also be effective in the instant invention.

The composition can be applied to the low carbon steel by a variety of methods. The composition can be applied by immersion of the low carbon steel or by spraying onto the steel surface. However, sufficient contact time between the composition and the steel surface must be made for the treatment to be effective.

20

The composition is best applied to the steel to be treated as an aqueous solution. It has been found that amounts as low as 10 parts per million parts of each component will form

- It is anticipated that the compositions and methods of the present invention would be effective for corrosion inhibition in cooling applications. The present invention also would eliminate the use of chromium for various treatments and thus is environmentally safer to use.
- Although the compositions of the present invention inhibit corrosion without other corrosion inhibitors present, they may also be used in conjunction with other additives to inhibit corrosion.
- In order to fore clearly illustrate this invention, the fath rat forth balos are doublepart. The fallowing examples are included as being illustrations of the invention and should not be construed as limiting the scope thereof.

Examples

Testing was conducted in a beaker corrosion test apparatus (BCTA) which employed linear polarization to measure the corrosion of low carbon steel in hils per year (mpy).

Testing was performed in the BCTA in a moderate hardness water at pH 8.4 with the following conditions:

250 ppm Ca (as CaCO₃) 200 ppm SO₄ 125 ppm Mg (as CaCO₃) 12 ppm SiO₂ 300 ppm Cl 166 ppm Na 80 ppm M alkalinity (as CaCO₃)

5

10

All test waters contained 1 ppm of hydroxyethylidene diphosphonic acid (HEDP) and 5 ppm of acrylic acid/allyl hydroxy propyl sulfonate copolymer for deposition control. These test results are presented in Table I.

TABLE I

1 Hour Contact Time

	Silicon Com-	H ₂ ZrF ₆	Passivation	Corrosion
5	pound (ppm)	(ppm)	рН	Rate(mpy)*
				56.1
	2731 ¹ ((100)	50	3.27	2.35
	2775 ² (100)	50	4.37	1.44
	2775 (50)	50	3.56	2.07
10	2775 (25)	25	3.83	2.88
. •	MTAS ³ (.25)	25	2.14	3.59
	21324 (100)	50	3.70	41
	EKY ⁵ (100)	50	3.65	43

- Averaged over 18 hour exposure to test solution.
- 15 l vinyl-trimethoxysilane, available as Huls 2781
 - 2 triaminopolytrimethoxysilane, available as Huls 2775
 - ${\bf 3}_{\rm methyltrimethoxysilane, available from Huls}$
 - 4 polydimethylsilane-polyokyalkylone, available as Masil 2132 from PPG Mazer
- 5 polyether modified dimethylpolysiloxane-copolymer, available as BKY 301 from BKY Chemie.

-8-

1

5

These results indicate the vastly improved differences between the inventive composition compared to the system which was not passivated. These results further indicate that the compositions of the instant invention prove effective at low dosages. Pretreatments 2132 and SKY proved ineffective as, although they are silicon compounds, they are stabilized silanes that possess ether bonding which makes them less easily approximately.

Other silicon compounds centaining easily hydrolyzable groups were tested with fluorozirconic acid under the same test conditions. These results are presented in Table II.

> ئىس. داراتە

TABLE 11

1 Hour Contact Time

5	Silicon Com- pound (ppm)	H ₂ ZrF ₆ (ppm)	PassivationpH	Corrosion Rate(mpy)*
	A (25) B (25) C (25)	50 25	3.85 3.5	5.43 2.78 2.1 (3.4)

- * Averaged over 18 hour exposure to test solution
- 10 A is sodium 3 (trihydroxysilyl) propylmethylphosphonate available as Q16083 from Dow Corning
 - B is sodium silicate R (ratio of $Si-O_2 \cdot N_{c_1}O$) = 1
 - C is sodium silicate R = 3.22

20

The present inventors anticipate that all soluble silicate compounds including sodium, potassium and lithium silicates would also be effective in the present inventive composition.

Testing was also performed in a bench-top test unit (BTU). This allows for the testing of "cold" surfaces through the coupons of a bypass rack as well as simulated heat exchange surfaces. Pretreatment was carried out directly in the BTU for one hour at 120° F with 50 ppm H_2ZrF_5 and 50 ppm of Dow's 2-6020 silane, designated N-($\mathcal B$ -aminoethyl) - $\mathcal Y$ - aminopropyltrimethoxysilane. After pretreatment, the silane solution was replaced with a water of the following matrix:

400 ppm Ca (as CaCO₃) 150 ppm Mg (as CaCO₃) 51 ppm Si-O₂ 244 ppm Na 284 ppm Cl 470 ppm SO₄ 205 ppm M Alkalinity (as CaCO₃)

l ppm HEDP and 5 ppm acrylic acid/allyl hydroxy propyl sulfonate copolymer were present as deposition inhibitors.

The heater wattage was set at $308^{0}F$, resulting in a skin temperature of $130^{0}F$. The sump temperature was $120^{0}F$. Results of this testing are reported in Table III.

<u> 14816 111</u>

BTU Testing

	And the second of the second	Cor Test 1 — Toy	rosion Rate Test 2 <u>mpy</u>	Test 3
15	Pretreated coupon (1 day)	11.5	10.4	
	Pretreated coupon (7 days)	5.2	2.1	2.0
20	Pretreated coupon (40 days)			0.8
	Non-pretreated coupon (1 day)	43		
25	Tube appearance	Clean Tube-out Day 7	Clean Tube-Out Day 16	Clean Tube-Out Day 40
			-	-

In all tests within two days the heat "transfer" tube developed the dark blue interference film. In Test 1 the tube was removed after 7 days, in Test 2 after 16 days, and in Test 3 after 40 days. In all tests, the heat exchange surface was clean with no indication of corrosion. The inventors anticipate that the localized heat on the surface of the tube actually enhances the tenacity of the film.

Comparative testing was performed against a known pretreatment inhibitor utilizing the BCTA. Water conditions were the came as those in Tables Land II. These results are presented in Table IV.

TABLE IV

	6 Hour Contact Time			
15 .	Treatment .	ppm	Passivation pH	Corrosion Rate(mpy)*
	1) Zinc Phosphate Prefilm	800	4.26	40
	Ca (as CaCO ₃)	170		
	Mg (as CaCO ₃)	110		
	2) 2775	100	4.49	5.43
20	H2ZrF5	50		
	3) 2775	100	4.42	7.31
	HzZrēs	50		

^{*} Averaged over 18 hour exposure to test solution

These results indicate the relative superiority of the silicon notecand fluorocincenic acid composition at inhibiting like carbon steel corrosion when compared to a known pretreating agent.

Table V presents results of testing in moderate hardness

water with the same conditions as in Table 1. These results indivicate that although the uses will inhibit composion by itself,
corrosion reduction is dramatically improved when the acid is will
in conjunction with an appropriate silvicon compound. Further, the
optimum pH of the passivation solution should be in the acid range
to achieve complete surface coverage of the film.

		TABLE V		
	Moderate Handress Water Treatment	1991	Passivation pH	Cornesian Rate(Tpr)*
15	1) HzZrf5	25	2.54	3.17
	2) Silicate M ₂ ZrF ₅	25 25	3.5	2.1
	3) Silicate HaZrfo	25 25	5.6	42.6

TABLE V (Cont'd)

Modera	te Haro	iness	Water
HOUE! a	ie naii	111622	Water

	Treatment	_pp=	Passivation pH	Corrosion Rate(mpy)*
5	4) 2775	50	6.98	61
	H ₂ ZrF ₆	25		
	5) 2775	25	3.83	2.88
	H ₂ ZrF ₆	25		

^{*} Averaged over 18 hour exposure to test solution

Table VI demonstrates that only complex fluoro acids are effective in the formation of the protective film on mild steel. The use of hydrofluoric acid (HF) does not promote film formation or offer protectica to mild steel.

TABLE VI

15	Moderate Hardness Water				
	Treatment	_pp::-	Passivation pH	Corrosion Rate(mpy)*	
	1) None		•••	56	
	2) 2775	100	5.0	5.5	
20	H2ZrF5	50			

-14-

TABLE VI (Cont'd)

Moderate Hardness Water		Daccia an	Corrosion
Treatment	_ <u>ppm</u>	<u>pli</u>	Rate * mpy
3) 2775	100	4.3	18
H2TiF6	50		
4) Z-6020	25	3	3.7
n ₂ 7eF ₃	25		
5) Z-6020	25	3.	84
HF	25		
	Treatment 3) 2775 H2TiF6 4) Z-6020 H270F2 5) Z-6020	Treatment ppm 3) 2775 100 H2TiF6 50 4) Z-6020 25 H2TiF : 25 5) Z-6020 25 25 25	Treatment ppm pit 1 3) 2775 100 4.3 H2TiF6 50 4) Z-6020 25 3 u2705. 25 5) Z-6020 25 3.

* Averaged over 18 hour exposure to test so

While this invention has been desc particular embodiments thereof, it is appropriate to the same and modifications of this inverto those skilled in the art. The appended invention generally should be construed to forms and modifications which are within the scope of the present invention. with respect to
that numerous
will be obvious
comes and this
are all such obvious
rue spirit and

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

- 1. A method of inhibiting the corrosion of low carbon steel surfaces in contact with an aqueous system comprising adding an effective amount of (a) a silicon compound containing a hydrolyzable group attached to a Si-O grouping and (b) a complex fluoro acid.
- 2. The method as claimed in claim 1 wherein said silicon compound is triamino polytrimethoxy silane.

- 3. The method as claimed in claim I wherein said silicon compound is vinyl-trimethoxy silane.
- 4. The method as claimed in claim 1 wherein said silicon compound is N-(β -aminoethyl) γ aminopropyltrimethoxysilane.
- 5. The method as claimed in claim 1 wherein said fluoro acid is fluorozirconic acid.
- 6. The method as claimed in claim 1 wherein said fluoro acid is fluorotitanic acid.
- 7. The method as claimed in claim 1 wherein said silicon compound and said fluoro acid are added to the steel in a carrier solvent.

- 8. The method as claimed in claim 7 wherein said solvent is water.
- 9. The method as claimed in claim 1 wherein said aqueous system is a cooling water system.
- 10. The method as claimed in claim 1 wherein said low carbon steel surfaces comprise the surfaces of a heat exchanger.
- 11. The method as claimed in claim 1 wherein said silicon compound and said fluoro acid are each added to said aqueous system in an amount ranging from about 10 parts to about 1000 parts per million parts aqueous system.
- 12. A low carbon steel corrosion inhibiting composition comprising a liquid carrier and dispersed or dissolved therein (a) a silicon compound containing a hydrolyzable group attached to a Si-O grouping and (b) a complex fluoro acid.
- 13. The composition as claimed in claim 12 wherein said silicon compound is triamino polytrimetnosy silane.
- 14. The composition as claimed in claim 12 wherein said silicon compound is vinyl trimethoxy silane.
- 15. The composition as claimed in claim 12 wherein said silicon compound is N-(β -aminoethyl)- β -aminopropyltrimethoxysilane.

- 16. The composition as claimed in claim 12 wherein said fluoro acid is fluorozirconic acid.
- 17. The composition as claimed in claim 12 wherein said fluoro acid is fluorotitanic acid.
- 18. The composition as claimed in claim 12 wherein said liquid carrier is water.

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☑ BLACK BORDERS	
☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES	
☐ FADED TEXT OR DRAWING	
BLURRED OR ILLEGIBLE TEXT OR DRAWING	
☐ SKEWED/SLANTED IMAGES	
☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS	
☐ GRAY SCALE DOCUMENTS	
LINES OR MARKS ON ORIGINAL DOCUMENT	
☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE PO	OOR QUALITY
OTHER:	

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.